Optimisation of the variational method for vibrational Hamiltonian eigenvalues computation

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abstract

We propose here an efficient method to define a representative approximation subspace to compute the first eigenvalues of the vibrational Hamiltonian which are those of interest in the experimental results. In the Born Oppenheimer approximation, calling by $\boldsymbol{x} = (x_1, \dots x_N)$ the dimensionless normal coordinates [4], ω_i the angular frequency associated with the coordinate x_i and $\hbar$ the reduced Planck constant, the vibrational Hamiltonian $\mathcal{H}$ writes as a sum of the nuclear kinetic and potential energies:

$$\begin{aligned}\mathcal{H}(\boldsymbol{x}) &= \mathcal{H}_0 + \mathcal{V} \\ &= \sum_{i=1}^{N} \frac{\hbar\omega_i}{2}\left(-\frac{\partial^2}{\partial x_i^2} + x_i^2\right) + \sum_{S_V \geq \|\mathbf{s}\|_1 \geq 3} K_{\mathbf{s}} \prod_{i=1}^{N} x_i^{s_i},\ \mathbf{s} = (s_1, \dots s_N).\end{aligned} \tag{1}$$

In (1) each monomial have a total degree $\|\mathbf{s}\|_1 \leq S_V$. The polynomial approximation of the potential energy is constituted by $\mathcal{V}$ and the second order monomials included in $\mathcal{H}_0$.

The eigenfunctions of $\mathcal{H}_0$ are pseudo-periodic signals vibrating at multiple level of fundamentals Harmonic frequencies. They write as

$$\phi^0_{\boldsymbol{n}}(\boldsymbol{x}) = \prod_{i=1}^{N} \psi_{n_i}(x_i),\ \text{for all } \boldsymbol{n} = (n_1, \dots, n_N), \psi_{n_i}(x_i) \text{ Hermite function of degree } n_i. \tag{2}$$

And the harmonic corresponding eigenvalues of $\mathcal{H}_0$ are

$$E^0_{\boldsymbol{n}} = \sum_{i=1}^{N} (n_i + \frac{1}{2})\omega_i\hbar. \tag{3}$$

Variational method in quantum mechanic is used to design a method that uses an adapted set of trial wave functions defining a subspace where the eigen-pairs of $\mathcal{H}$ are computed.

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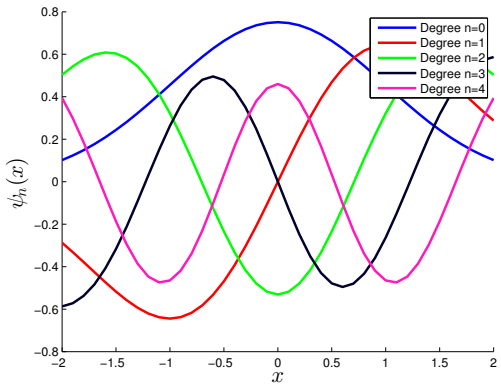

Figure 1: First hermite functions from degree 0 to 4

The eigenfunctions of $\mathcal{H}_0$ (2) constitute a well-suited approximation space. Indeed, when looking at the form of the operator $\mathcal{H}$ (1) we see that $\mathcal{H}_0$ already contains Kinetic energy and the quadratic terms of the potential energy faithfully representing its behaviour in a localized area around equilibrium. In other words, $\mathcal{H}_0$ is the zero order approximation of $\mathcal{H}$.

In order to deal with the curse of dimensionality that rapidly Happens because of the product space structure of the approximation space, we propose a basis selection technique based on perturbational theory [3].

This technique is in the context of vibrational configuration interaction with perturbation selected interactions [2, 1].

Calling by $\|\mathcal{V}\|_2$ the spectral norm of the operator $\mathcal{V}$, the first eigenvalues of $\mathcal{H}$ are considered perturbation of the first harmonic eigenvalues because

$$\|\mathcal{V}\|_2 = \epsilon * \|\mathcal{H}_0\|_2, \ \epsilon < 1. \tag{4}$$

Actually, the value of ϵ depends on the distance with the ground state and then constitute relevant information for the selection of the minimal required sub basis for the computation of the eigen-pairs of $\mathcal{H}$.

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